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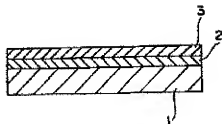
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(54) COATED PLATE WITH HIGH RESISTANCE TO POLLUTION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a coated plate bearing a coating which is formed from a coating material cured and dried at normal temperature and, at the same time, curable by thermal promotion at relatively low temperature and has high surface hardness, weather resistance, durability, and especially high pollution resistance for a long duration.

SOLUTION: This coated plate has a primer layer 2 of an epoxy type primer coating material formed on a substrate 1 and an upper coating layer 3 formed on the primer layer 2 of an upper coating material containing an oligomer solution in which silica of organosilane produced by partial hydrolysis of the hydrolyzable organosilane in colloidal silica is dispersed, polyorganosiloxane containing silanol group, a linear polysiloxane containing hydroxyl groups in both terminals, and a curing catalyst.



NOTICES *

JP 09-141193A [CLAIMS]
* NOTICES *

1. This document has been translated by computer. So the translation may not reflect the original precisely.

2. * shows the word which can not be translated.

3. In the drawings, any words are not translated.

CLAIMS

[Claim 1] It has the primer layer formed from an epoxy system primer paint on the surface of a base material. A finishing coat formed in the surface of this primer layer from top coat coated plate which it has, and said top coat, (A_1) General formula R^1-SiX_3-m (among a formula) A monovalent hydrocarbon radical of substitution same [R^1] or of a different kind or the unsubstituted carbon numbers 1-9 is shown, and an integer of 0-3 and X shows a hydroxylic organic silane. A hydroxylic organosilane expressed in colloidal state, dispersed in an organic solvent water, or those mixed solvents. A silica dispersed oligomer solution of an oligomers which carries out partial hydrolysis under conditions which use water 0.001-0.5 mol per said 1 Et of hydroxylic basis OH_2 , (B_1) Average composition formula $R^2-Si(OH)_2$ ($4-m-n$) / 200 (among a formula) A monovalent hydrocarbon radical of substitution same [R^2] or of a different kind or the unsubstituted carbon numbers 1-9 is shown, and a and b are numbers which fill a relation of $0.2 \leq a/b \leq 2$, $0.0001 < b < 3$, and $a+b < 4$, respectively. Polyorganosilane which is expressed and contains a silanol group in a molecule, (C_1) Empirical formula $HO(R^3)_2SiO_2$ (H) (m) (among a formula) R^3 — said formula (H) — the same as an inner thing — n — three or more integers. With a straight-chain-shape both-ends hydroxyl group content polysiloxane (straight-chain-shape polydimethylsiloxane) expressed, (D_1) Including a curing catalyst, inside of the aforementioned (A_1) ingredient. Said silica is contained five to 95 weight % as solid content, and said at least 50-mole of hydroxylic organosilane is an organosilane of $m=1$. While the 99 to 100 weight % of aforementioned (B_1) weight section is blended to the one to ingredient 99 aforementioned (A_1) weight section. (However, the total quantity of an ingredient (A_1) and an ingredient (B_1) is 100. It is a weight section.) A contamination-resistant coated plate which contains 0.1 to 70 weight % of the aforementioned (C_1) ingredient to the above (A_1), (B_1) and (D_1) sum total content of an ingredient.

[Claim 2] The contamination-resistant coated plate according to claim 1 in which said base material is an organic cured body.

[Claim 3] The contamination-resistant coated plate according to claim 1 in which said base material is a metal plate.

[Claim 4] The contamination-resistant coated plate according to claim 1 in which said base material is a water glass decorative sheet.

[Claim 5] The contamination-resistant coated plate according to claim 1 in which said base material is a plastic-molding board.

[Claim 6] A contamination-resistant coated plate given in either from Claim 1 in which said epoxy system primer paint is an epoxy resin primer paint to 5.

[Claim 7] A contamination-resistant coated plate given in either characterized by comprising the following from Claim 1 to 5.

Said epoxy system primer paint is epoxy resin (A_1) and/or siloxane resin modified epoxy resin 100 weight section.

[B_1] At least one hydroxylic basis combined with a silicon atom.

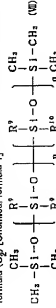
One to hydroxylic organic silicon compound 400 weight section which has at least one isocyanate group and/or an isocyanate ring which were combined with a silicon atom via at least one carbon atom.

(C_1) 0.01 to curing catalyst 30 weight section, and general formula (C_1) $R^3-R^3SiX_2$ (m) (R^3 and R^4 among a formula) Expressing a univalent hydrocarbon group independently, respectively. Y expresses a univalent

hydroxylic basis. A hydroxylic JIORGANO silane expressed and/or its one to partial hydrolysis condensate 300 weight section

[Claim 8] Said epoxy system primer paint (A_1) a ethylene type monomer 99.5 - 75-mol %, (b) General formula R^5SiX_3-n (n) (V) (among a formula) R^5 expresses a univalent hydrocarbon group containing a vinyl group, and R^5 expresses a univalent hydrocarbon group of the carbon numbers 1-10, and X , A basis selected from groups which consist of an alkoxyl group of the carbon numbers 1-4, an alkoxyl alkoxy group of the carbon numbers 2-6, and an oxime group of the carbon numbers 2-4 which can be hydrolyzed is expressed, in expression an integer of 1-3, 0.5-20 mol of unsaturation group content silicon compound % expressed. A hydroxylic basis content vinyl system copolymer produced by making carry out copolymerization, and a (B_2) a) bisphenol A-epichlorohydrin system epoxy resin, (d) General formula (R^7)

$Si(OH)_2$ (n) (N) (among a formula) R^7 expresses a univalent hydrocarbon group which is mutually the same or different. R^8 expresses a hydrogen atom or a univalent hydrocarbon group, a is the number of 1.0-1.7, b is the number of 0.05-0.2, and c is the number expressed with $(4-a-b) / 2$, c is two or more numbers. Epoxy desaturation siloxane resin obtained by making polyorganosiloxane expressed react, and a general formula (C_2) [Chemical formula 1]



(R^9 among a formula a univalent hydrocarbon group which is mutually the same or different) [express and] R^{10} expresses a univalent epoxy functional organic group, p is an integer of 0-100, and q is an integer of 1-100. A contamination-resistant coated plate given in either from Claim 1 containing epoxy modified siloxane oil expressed and an organic solvent (D_2) to 5.

[Translation done.]

[0038] Especially the epoxy modified silicone oil that is the aforementioned (C₂) ingredient is obtained by carrying out the addition reaction (hydroxylation) of the olefin nature epoxy monomer to a polyvinyl ether siloxane, for example, without not necessarily limit. The amount of the epoxy modified silicone oil used is 0.1 to 50 weight % of within the limits to the sum total solid content of the aforementioned (A₂) ingredient and an ingredient (B₂) preferably, although limitation in particular is not carried out. If sufficient adhesion with a base material is not acquired as it is less than 0.1 weight %, but it exceeds 50 weight %, the hardenability of a primer will fall.

[0037] As an organic solvent used as the aforementioned (D₂) ingredient, although limitation in particular is not carried out, for example methyl alcohol, ethyl alcohol, alcohols, such as isopropyl alcohol, ethylene glycol monomethyl ether, ether, acetone or ketone, such as ethylene glycol monomethyl ether, a diethyl ketone, methyl tetrahydrofuran, and dioxane. Aromatic solvents, such as methyl ethyl ketone and an ethyl acetate; Methyl acetate, aliphatic hydrocarbon, such as *n*-hexane, such as ethyl acetate and *n*-butyl acetate, gasoline, a rubber solvent, a mineral spirit, and kerosene; aromatic hydrocarbon, such as benzene, toluene, and xylene, is mentioned.

[0038] The amount of the aforementioned (B₂) ingredient used has preferred within the limits of ten to 5000 weight % section to the ingredient 100 aforementioned (A₂) weight section, although limitation in particular is not carried out. Since it will be necessary to give two coats repeatedly if workability falls and 5000 weight sections are exceeded, since the viscosity of a primer paint will become high there is less amount used than 100 weight sections, workability falls too.

[0039] A curing catalyst can be used to harden at ordinary temperature when you want to burn for a short time, the case where he would like to print comparatively the 3rd epoxy system primer paint containing these (A₂) (B₂), (C₂) and an ingredient (D₂) at low temperature, and. As for the amount of the curing catalyst used, although limitation in particular is not carried out, it is preferred that they are less than 30 weight % section to the ingredient 100 aforementioned (A₂) weight section. If the amount of the curing catalyst used exceeds 30 weight sections, foaming is produced at the time of baking of a primer paint, or a curing catalyst will ooze on the surface of primer cured coating, and an adhesive property with finishing coat will be checked. Although limitation in particular is not carried out, as an example of a curing catalyst Diisobutyl diacetate, Diisobutyl diacetate, a butyltin bird (2-ethylhexoate). The 1st tin of caprylic acid, naphthenic acid tin, oleic acid tin, iron-2-ethylhexoate, Organic-carboxylic-acid metal salt, such as naphthenic acid titanium, zinc naphthenate, cobalt naphthenate, and zinc stearate; Tetraethyl titanate, Tetra (2-methylhexyl) titanate, lithium aluminum titanate, Organic titanium acid ester, such as tetra (isopropenyl) titanate; ORGANO allyl titanium, Organic titanium compounds, such as beta-carboxy titanium (isopropenyl) tin; triethoxy titanium, Organic amino-group substitution alkoxyalane, such as N-trimethylsilyl (isopropenyl) triethoxyalane; Hexylamine, amino compounds, such as phosphoric acid doctylamine, or salt; — 4th ammonium salt [such as benzyl triethyl ammonium acetate]; — potassium acetate and sodium acetate. The lower-fatty-salt salt of alkaline metals, such as a lithium oxalate; Dimethylhydroxyamine, Dialkyl hydroxyamine, such as diethylhydroxyamine; guanidine compounds, such as tetramethyl guanidine, and guanidyl group content Silane, or a siloxane compound can be mentioned.

[0040] Said 3rd epoxy system primer paint may contain further other pigments, such as titanium oxide, carbon black, and iron oxide, a varnish and ultraviolet absorber, antioxidant, an ultraviolet ray absorber, a drying stop agent, etc. If needed. Silica distribution oligomer which is an ingredient (A₂) of the top coat used by this invention. To for example, the colloidal silica distributed by an organic solvent or water (the mixed solvent of an organic solvent and water) is also included. One sort of the hydroxy-0.001-0.5 organosilane expressed with said general formula (D) or two sorts or more are suited. It is 0.001-0.5 per said 1 Eq of hydrolytic basis (O) about the water of the water added to the primer paint. It is obtained by carrying out partial hydrolysis of the hydrolytic organosilane under the conditions which use a metal.

[0041] A basis R¹ in the hydrolytic organosilane expressed with said general formula (D). Although limitation in particular is not carried out, for example A methyl group, an ethyl group, an isopropyl group, Alkyl groups, such as a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, A cycloalkyl group, Cycloalkyl groups, aliphatic groups, such as 2-methylpropyl group, An alkyl group, such as 2-pentyl group, 3-methylpropyl group, A phenyl group, Aryl groups, such as a tolyl group; Alkenyl group, chloromethyl groups, such as a vinyl group and an allyl group, Halogenation hydrocarbon-

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group, gamma-methoxyloxypropyl groups, such as gamma-chloropropyl group and a 3,3,3-trifluoropropyl group, Substitution hydrocarbon groups, etc. can be mentioned. Also, a 3,4-epoxydichloropropyl group, a 3,4-epoxydichloropropyl group, etc. can be mentioned. Also, in these, the alkyl group of a phenyl group, and gamma-mercaptopropyl group, etc. can be illustrated. Also in these, the alkyl group of a composite case or the case of acquisition to the carbon numbers 1-4 and a phenyl group are preferred. [0042] Although limitation in particular is not carried out as said general formula (I) Naka and the hydrolytic basis X, an alkoxyl group, an acetoxy group, an oxime group, an ENOKISHI group, an amino group, aminoxy, an amide group, etc. are mentioned, for example. Also in these, since it is easy to prepare an ease of acquisition, and a silica distribution organosilane oligomer solution, an alkoxyl group is preferred.

[0043] As an example of said hydrolytic organosilane, The alkoxyalane of each functionality of mono-, di-, tri-, and tetra- whose m of said general formula (I) Naka is a hydrolytic basis of 0-3, acetoxyalane, oxime silane, hydroxy pendant fur, oxime silane, aminoalane, furan N-oxime silane, and amino silane, mentioned. Also in these, since it is easy to prepare an ease of acquisition, and a silica distribution organosilane oligomer solution, a silica distribution organosilane oligomer solution is preferred.

[0044] Especially as tetra alkoxyalane of m = 0, Can illustrate a tetramethoxy silane, a tetraethoxyalane, etc. and as organosilane alkoxyalane of m = 1, Methyl trimethoxy silane, methyl triethoxy silane, a methyl trimethoxy silane, phenyltrimethoxy silane, phenyltriethoxy silane, 3 and 3, 3-trifluoromethyl trimethoxy silane, etc. can be illustrated. As a JORIGANO dialkoxyl silane of m = 2, Dimethylmethoxy silane, dimethyl diethoxy silane, diphenyldimethoxy silane, Can illustrate diphenyl diethoxy silane, methylphenyl trimethoxy silane, trimethyl isopropoxy silane, dimethylphenyl methoxy silane, etc. can be illustrated. An organosilane compound generally called a silane coupling agent is also contained in alkoxyalane.

[0045] The heads of the hydrolytic organosilane expressed with said these general formula (I)s, and more than 50 mol % — desirable — 80 mol % — the above — more — desirable — 70 mol % — the above is functional [which is expressed with m = 1]. This is 0.001 silica in the aforementioned (A₂) ingredient, hardness sufficient in the following is not obtained. As colloidal silica in the aforementioned (A₂) ingredient, although limitation in particular is not carried out, it can use organic solvent dispersible colloidal silica of non-drainage systems, such as water dispersibility or alcohol, for example. Generally, such colloidal silica of 20 to 50 weight % about the silica as solid content. It contains and silica loadings can be determined from this value. When using water dispersible colloidal silica, the water which exists as ingredients other than solid content can be used for hydrolysis of said hydrolytic organosilane. Water dispersible colloidal silica can usually be easily obtained as a commercial item, although made from water glass. Organic solvent dispersible colloidal silica can be easily prepared in replacing the water of said water dispersible colloidal silica by an organic solvent. Such organic solvent dispersible colloidal silica as well as water dispersible colloidal silica can be easily obtained as a commercial item, although made from water glass.

[0046] Colloidal silica can be used for hydrolysis of said hydrolytic organosilane. Water dispersible colloidal silica can be easily obtained as a commercial item, although made from water glass. Organic solvent dispersible colloidal silica can be easily prepared in replacing the water of said water dispersible colloidal silica by an organic solvent. Such organic solvent dispersible colloidal silica as well as water dispersible colloidal silica can be easily obtained as a commercial item, although made from water glass. Ethylene glycol, isopropanol, toluene, ethyl acetate, methyl acetate, butyl acetate, and isobutanol. Ethylene glycol, ethylene glycol, ethylene glycol monomethyl ether, and acetic acid ethylene glycol monomethyl ether. A diethylene glycol, Diethylene glycol derivative [such as diethylene glycol monomethyl ether, 1,4-dioxane alcohol, etc. can be mentioned, and one sort chosen from the group which consists of these, or two sorts or more can be used. It can use together with these hydrophilic organic solvents, and toluene, xylene, ethyl acetate, butyl acetate, methyl isobutyl ketone, methyl ethyl ketone, etc. can be used.

[0047] Colloidal silica is [be / is / under / aforementioned (A₂) ingredient / setting /] a part for silica (weight which converted content Si into SiO₂). It is considered as solid content and contains by 20 to 80 weight % of within the limits more preferably ten to 50 weight % five to 95 weight %, If content is less than 5 weight %, desired film hardness will not be obtained, but on the other hand, when 95 weight % is exceeded, the uniform dispersion of silica may become difficult and an ingredient (A₂) may gel.

[0048] 0.001-0.5 per said 1 Eq of hydrolytic basis (O) in which said hydrolytic organosilane has the quantity of the water used when preparing silica distribution oligomer which is the aforementioned (A₂) ingredient as mentioned above is it within the limits which is a mol. The amount of the water used is 0.001. If sufficient partial hydrolysis is not obtained as it is less than a mol, but 0.5 mol is exceeded, the stability of a partial hydrolysis, for example. What is necessary is not to limit the method in particular of carrying out partial hydrolysis, will worsen. What is necessary is to mix a hydrolytic organosilane and colloidal silica, and just to carry out addition combination of the case of an initial complement, and a partial hydrolytic reaction solution, at ordinary temperature in that order. In order to promote a partial hydrolytic reaction Chloride, acetic acid,

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halogenation. Silane, organic acid and inorganic acid, such as chlorosulfonic acid, citric acid, benzoic acid, dimethylmalonic acid, formic acid, propionic acid, a glutaric acid, glycolic acid, maleic acid, malonic acid, toluenesulfonic acid, and oxalic acid may be used as a catalyst.

[0048]In order that the aforementioned (A_2) ingredient may obtain the performance by being stabilized over a long period of time — the pH of fluid — desirable — 20–7.0 — more — desirable — 2.5–6.5 — — it is good to use 3.0–4.0 still more preferably. Especially the amount of the water used is 0.3 per hydroxyloxy basis (X) 1 equivalent as pH is outside this range. The f_2 of the performance durability of an ingredient, (A_2) is remarkable under the conditions more than a mol. (f_2) What is necessary is for what is necessary to be to add basic reagents, such as ammonia and hydroxide, and just to adjust pH, if it is in acidity and just to adjust pH using acid reagents, such as chloride, nitric acid, and acetic acid, from this range, if it is a basicity side when pH of an ingredient is outside a mentioned range. However, the adjustment method in particular is not limited.

[0049]As R^2 in said average composition formula (D) of the silanol group content polyorganosiloxane used as the aforementioned (B_2) ingredient, it is not carried out but especially limitation is said formula (D).

Although the same thing as inner R^1 is illustrated, desirable — substitution hydrocarbon groups, such as the alkyl group of the carbon number 1–4, a phenyl group, a vinyl group, gamma-glycidyloxy propyl group, gamma-methacryloxypropyl group, gamma-aminopropyl group, and a 3,3,3-trifluoropropyl group, — they are a methyl group and a phenyl group more preferably. The results of said formula (D), and a and b are numbers which fit the aforementioned relation, respectively, and is a 0.2. If the following of a exceeds 3, it will be easy to produce a crack in coated coating. When it is four or less [2 or more], hardening of 0 does not occur well by less than 0.0001. Polyorganosiloxane, although not necessarily limited especially — the aforementioned (B_2) ingredient group compounds, siloxane, dimethylsiloxane, and diphenyl disiloxane — or, it can obtain by hydrolyzing one sort or two sorts or more of mixtures of siloxane corresponding to these with a lot of water by a publicly known method. In order to obtain silanol group content polyorganosiloxane, when siloxane is used and it hydrolyzes by a publicly known method, the alkyl group which is not hydrolyzed may remain in a minute amount. That is, in this invention, although the polyorganosiloxane that a silanol group and a little alkyl groups live together may be obtained, even if it uses such polyorganosiloxane, it does not interfere.

[0051]Said empirical formula (D) showing the straight-chain-shape both-ends hydroxyl group content polyorganosiloxane (straight-chain-shape polyorganosiloxane) which is the aforementioned (B_2) ingredient — inside, although n is as aforementioned, it is within the limits of 10–200 (about about, 1000 to 20000 weight average molecular weight) preferably. As a curing catalyst, which is the aforementioned (C_2) ingredient, for example, alkyl titanates, Tin octylates, dibutyltin dilaurates, Carboxylic acid metal salt, such as decyl tin carboxylate, alkyl amine 2 — HEXISOETO, Carboxylic acid quaternary ammonium salt, such as amine salt, carboxylic acid tetramethylammonium salt, such as dimethylamine acetate and tetramethylammonium acetate, such as triethyl trimellitate, Amine system amine coupling agents, such as N-beta-dimethoxyethyl gamma-aminopropyl triethoxysilane and N-beta-dimethoxyethyl gamma-aminopropyl methyl dimethoxysilane, P-toluenesulfonic acid, Aluminum compounds, such as oxides, aluminum alkoxides, such as phthalic acid and chloride, and aluminum olefates; The alkali catalyst of a potassium hydroxide salt, Titanium compounds, such as tetraisopropyl titanate, tetrabutyl titanate, and titanium tetra acetylacetonate; halogenation Silane, such as methylchlorosilane, dimethyldichlorosilane, and trimethylchlorosilane, is mentioned. However, if effective in condensation of the above (A_2), (B_2), and (C_2) an ingredient, there will be no restriction in particular.

[0052]A blending ratio between the aforementioned (A_2) ingredient and the aforementioned (B_2) ingredient is as aforementioned. (A_2) if there are too many blending ratios of an ingredient, it will be easy to produce a crack on a film, and if too small sufficient room temperature-setting performance and film hardness will not be obtained. Loadings of the aforementioned (B_2) ingredient are within the limits of the above. When loadings are less than said range, a contamination-resistant manifestation is weak, if it exceeds said range, hardness will not advance well, therefore a film will become soft.

[0053]An addition of the aforementioned (B_2) ingredient is the total quantity 100 of the aforementioned (A_2) ingredient and the aforementioned (B_2) ingredient is a total quantity 100 of the aforementioned (A_2) ingredient and the aforementioned (B_2) ingredient. Although limitation in particular is not carried out as opposed to a weight section, Within the limits of 0.0005 to 8 weight section is [within the limits of

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0.0001 to 10 weight section [within the limits of 0.0007 to 5 weight section still more preferably more preferably. When an addition is not limited at ordinary temperature at less than 0.0001 weight sections and 10 weight sections are exceeded, heat resistance and weatherability may worsen.

[0054]T top coat used by this invention can be diluted and used with various organic solvents. In order to make the handling easy, Although a kind of organic solvent used can be selected with a kind of monovalent hydrocarbon radical of each ingredient, or a size of a molecular weight and limitation in particular is not carried out, said top coat may be added if needed. As paints which can be added, although limitation in particular is not carried out, for example Carcure black, it does not interfere, even if inorganic pigments, such as organic colors, such as Quinacridone, naphthol red, cyanine blue, cyanine green, and Hansa yellow, titanium dioxide, barium sulfate, or two sorts or more, and a composite metal oxide, are good and use it constituting one sort or more than these groups, or more. What is necessary is just to perform addition of paint by the usual method. In that case, use of a dispersing agent, a distributed solvent, a drying agent, a thickening agent, a coupling agent, an ultraviolet ray absorber, etc., may be added if needed.

[0055]Although for the thickness of the film formed from said top coat not to have restriction in particular and what is necessary is just 0.1 – 200 nm, in order to be stuck to a film, to hold it stably in the long run and for neither a crack nor exfoliation to occur, 10 – 100 nm is preferred. Said top coat can be coated with the usual coating method, for example, can choose the various coating methods of brush coating, spray, immersion, a flow, a roll, a curtain, a knife coat, etc. Rastercoat. In particular does not have a dilution rate in an organic solvent, it should just determine a dilution rate if needed.

[0057]Although said top coat can be processed at ordinary temperature, heat cure of it may be carried out from relations, such as a production process of a coated plate, if needed. Baking temperature in that case has preferred within the limits of 40 – 200 °, although limitation in particular is not carried out. In a coated plate concerning this invention, since finishing coat is formed from top coat containing said specific ingredient, resistance to contamination excellent in a coated plate is given.

[0058]A straight-chain-shape both-ends hydroxyl group content polyorganosiloxane (straight-chain-shape polyorganosiloxane) which is an ingredient (C_2) gives resistance to contamination excellent in a film formed especially among ingredients contained in said top coat. Since this (C_2) ingredient does not have any reaction groups other than an OH radical, it is a molecule comparatively lacking in reactivity.

Therefore, since perfect compatibility in inside of a paint is missing and it is distributed as an ultrathin particle, it carries in a paint film surface easily, and a monomolecular layer is formed, but eventually, the OH, carries out a condensation reaction to OR group of bulk, and remains in a paint film surface. As a result, since a R^2 group covers a paint film surface and a pollutant (a gas, a solid, a liquid) is not allowed to come near, resistance to contamination is raised by leaps and bounds. Since a R^2 group has covered a paint film surface, even when a pollutant adheres it adheres to it easily (decontamination nature is high), and a mold-release characteristic over adhesives is given. Therefore, while being able to remove dirt, dust, etc., such as adhesion and scorable, easily, there is an effect also in prevention of a poster etc. Said empirical formula (D) of an ingredient (C_2) inner n is able for a large thing to form a layer in a paint film surface in a small quantity. On the other hand, it gives pliability to a coat by it not only forming a layer, but a small thing having the high reactivity of an OH radical and being easily incorporated into a crack in a paint film surface, and it leads also to a crack preventive effect. Therefore, a crack where a crack could not enter easily and which was excellent in resistance to contamination by blending optimum doses with top coat from a large thing of n to a small thing as an ingredient (C_2) is formed.

[0059]Said top coat contains (A_2), (B_2), and (D_2) an ingredient in addition to an ingredient (C_2). Silica distribution oligomer which is an ingredient. On the occasion of film formation, become the hydrophobic base as a functional group best for a hardening reaction the main ingredients of this hydrophobic base, has, and colloidal silica is (A_2) ingredient. While making hardening of the film formed high, improve the smooth nature of a film, and crack resistance and the silanol group content polyorganosiloxane which is (B_2) ingredient (A_2) With an ingredient and (C_2) an ingredient, carry out a condensation reaction and it participates in curing coating formation. The smooth nature, the mechanical strength, and toughness of a film are raised, and the curing catalyst which is (D_2) ingredient promotes the condensation reaction of the

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above (A.), (B.), and (C.) an ingredient, and stiffens a film.

(2006) The hydrolytic basis contained in silica distribution oligomer which is the aforementioned (A_2) ingredient, and the silanol group in the above (B_2) and (C_2) an ingredient, in ordinary temperature, by carrying out a condensation reaction is carried out and cured coating is formed. Therefore, unlike the ordinary existence of the curing catalyst which is the aforementioned (D_2) ingredient, the constituents for curing conventional moisture curing type, said top coat containing these ingredients is hardly influenced by humidity, also when hardening at ordinary temperature. When heat-treated, a crosslinking reaction is promoted and cured coating can be formed.

[0006] In the coated plates concerning this invention, since the primer layer which intervenes between the finishing coat and a base material is formed from an epoxy system primer paint, the resistance to contamination of a coated plate and adhesives are maintained in the long run. Adhesive strength and chemical resistance (when the said 2nd or 3rd epoxy system primer paint is used especially as a primer paint which forms a primer layer) of a primer layer the adhesion according to the reaction of a hydrolytic basis to these, and the endurance of silicone — being added — the long-term adhesion of a base material on a plate, and the endurance of a plate on a primer layer, and the long-term maintenance of the long-term resistance to contamination of a coated plate and endurance as a result.

[0007]

(Mode for carrying out the invention) Drawing 1 expresses one embodiment of the contamination-resistant coated plate concerning this invention. This coated plate has the primer layer 2 formed in the surface of the base material 1 from the epoxy system primer paint. It has the finishing coat 3 formed in the surface of this primer layer 2 from the two coat containing the above (A), (B), (C), and (D), an inorganic

[0063] Although the concrete embodiment and comparative example of this invention are shown below, this invention is not limited to the embodiment stated to the following embodiment and the top. Below, all "parts" show a "weight section" and expresses "weight % all %".

— Embodiments 1-8 — [Production of a contamination-resistant coated plate] The contamination-resistant coated plate was produced using the material and the method which are shown below.

Base material—The Nozawa flexible sheet by Nozawa Corp. (the fiber reinforced cement plate within JIS-A5430 standard; flexible board 910x2420x6 mm).

[0064]
Base-material-2: A commercial rolled plate (Japanese Test plate purchase; JIS-G3101 conformity; 910x2420x3 mm).

Base-material-3: Asano Slate Co., Ltd. make Asano tie RAKKUSU FA-T (the board which stained water ofase on the slate plate: 1210x1820x4 mm).

Base-material-4: Teijin Chemicals PC-1111 (polycarbonate sheet; 1000×2000×3 mm).

(Primer paint)
[Base material-V. Dullish gray clay inclusion, no. polyacrylate emul.]

Primer 1: EPORO E sealer (ISAMU PAINT CO., LTD. make; two-component type epoxy resin sealer).

Resin 2: EPOBO 2 (epimer) (ISAMI PAINT CO. LTD. make; two-component type epoxy resin primer).
[0066]

The primer which consists of $-(A_1-1)$ (D₁-1) ingredient and the organic solvent below Primer 3: (40% of active principle: viscosity of 5.0 cps; reddish brown transparency).

(A.-1) : Epicoat 828 (trade name of ShellChemical; weight per epoxy equivalent 190) 100 copy.

10057

(B₁-1): N,N,N-tris 3-(trimethoxysilyl) propyl 100 copies of isoSHIANURATO.

($C_1 - 1$): the first four copies of tin of octanoic acid.
($D_1 - 1$): 100 copies of dihydromethoxyresilane.

Organic solvent: 760 copies of toluene.

100 copies of ingredients (A_{n-1}) and (B_{n-1}) 7.5 copies of ingredients which were obtained with the

preparing method below Primer 4; 2.5 copies of following (C_2-1) ingredients and 50 copies of ingredients ($D-1$), and a mixture with one copy of curing catalyst.

(A_2 - V_1) to the reaction vessel provided with the stirrer, the condenser, and the thermometer (preparation of A_2 - V_2). Polymerized by heating for 8 hours at 70 °C in a nitrogen gas atmosphere, having added 1.3 g of an ingredient (copolymerized with 100 copies of methyl methacrylate, 13.1 copies of 3-methoxystyrene, 10.3 copies of isobutylacrylate as 100 copies of methyl methacrylate). 13.1 copies of 3-methoxystyrene, 10.3 copies of isobutylacrylate, 22.2 copies of toluene, and a polymerization initiator, and stirring uniformly. Subsequently, the polymer solution (A_2 -1) (ingredient) which is a water-white liquid was obtained by distilling a nonvolatile matter to 50% by distilling off part of toluene with a low fraction.

[illegible]

denaturation silicone of said structural-formula (VII) (however, $R^2=CH_3$, the epoxy functional organic group of the formation 4 of the bottom type of $R^{10} =$ p**33, g**32).

[0071]

[Chemical formula 4]

$$\text{Cl}_2\text{CH}-\text{CHCl}-\text{OOC}-\text{CH}(\text{OOC}-\text{CHCl}-\text{CHCl}_2)-\text{CHCl}_2$$

[0072]
Ingredient: (D,-1) Ethyl acetate.

Curing catalyst: dibutyltin dilaurate

Primer 1: Air spray painting (coat

[0073]

Primer 3: Air spray painting (coat

Primer 4: Air spray painting (coat

(dry curing method of a primer
about 20 ** and one day).
(Top coat) The example of the primer

[0074](A₂) (example of preparation of an ingredient)

(λ_0) in an agitator and warning — in the flask furnished with a jacket, a capacitor, and a thermometer (preparation of an 30% methanol distribution dibutyl silicon — sol — MA-57 (the particle diameter 10–20 — in micro) 30% of solid content, moisture 0.5% Nissan Chemical Industries, Ltd. made 100 parts of methyl trimethoxysilane, and water 2.7 After performing a partial hydrolysis reaction over about 5 hours at the temperature of 65 °C, supplying and stirring a part, the hydrogel was obtained by cooling (the λ_0 1.5). Solid content when this thing was allowed to stand at the room temperature for 48 hours was 30%. [0075]

(A_0-1) preparation conditions of an ingredient: - Number of mols $0.1 - (A_0-1)$ of the water per 1 Eq of hydrolytic bases Silioa part content of an ingredient Mol % 100 of the hydrolytic basis content organosilane

(ingredient) was obtained by distributing 20 copies of white pigments ("R820" by Ishihara Sangyo Kaisha, Ltd.) in 100 copies of aforementioned (A_0-3) ingredients.

(A_0-3) an agitator and warming — in the flask furnished with a jacket, a capacitor, and a thermometer (preparation of an ingredient), isopropyl alcohol distribution colloidal silica — sol — IPA-st (the particle diameter 10–20 — m micro) 30% of solid content, moisture 0.5 %, Nissan Chemical Industries, Ltd. make 100 copy, 88 copies of methyl triisopropylsilane, 18 copies of dimethylmethoxysilane, and water 1 A part and 80 cc, anhydride 0.1. After performing a partial hydrolysis reaction over about 3 hours at the temperature of 80 °C, supplying and stirring a part, the reaction mixture was obtained by cooling. Solid content when this thing was allowed to stand at the room temperature for 48 hours was 38%. The brown paint (A_0-3) (ingredient) was obtained by distributing 15 copies of brown pigments (MN-V by Tōdō Kogyo Corp.) with a paint shaker in 100 copies of this reaction mixture.

[0076]

(A_0-3) preparation conditions of an ingredient: the number [] of mole of the water per 1 Eq of hydrolytic bases — silica part content [] of 0.3 and (A_0-3) an ingredient — mol % 77-mole of the hydrolytic basis content organopoloxane of 40.2% and m=1 — next, (B_2) . The example of the preparing method of an ingredient is as follows.

[0077][B₂] (example of preparation of an ingredient)

(B_2-1) an agitator and warming — a jacket and a capacitor — (preparation of an ingredient). A mixture of methyl triisopropylsilane 220 part (1 mol) and toluene 150 part is taught to a flask furnished with a dropping funnel and a thermometer, and it is the 1% hydrochloric acid aqueous solution 108 to this mixture. A part was dropped over 20 minutes and a methyl triisopropylsilane was hydrolyzed. When stirring was stopped 40 minutes after dropping, it separated into a bilayer. Mixed liquor of lower layer water and isopropyl alcohol having contained a small amount of chlorides is separated. After washing in cold water removing alcohol which remains in a resin solution of toluene which remained behind and carrying out decompression removal of the toluene further, by diluting with isopropyl alcohol. An isopropyl alcohol 4% solution (B_2-1) (ingredient) of silanol group content organopolysiloxane of the weight average molecular weight 2,000 [about] was obtained.

(B_2-2) By the same operation as a preparing method of the aforementioned (B_2-1) ingredient, a toluene solution of silanol group content organopolysiloxane was obtained except having changed the last diluent solvent into toluene (preparation of an ingredient). Then, a toluene 40% solution (B_2-2) (ingredient) of silanol group content organopolysiloxane of the weight average molecular weight: 10,000 [about] was obtained by performing a dehydrating condensation reaction of silanol group content organopolysiloxane at temperature of 150 °C for 12 hours.

(B_2-3) an agitator and warming — a jacket and a capacitor — (preparation of an ingredient). To the flask furnished with a dropping funnel and a thermometer, it is the water 1,000. Part. Prepare 50 copies of octadecane and further 44.8 copies (0.3 mol) of methylchlorosilanes. It is the toluene 200 about 38.7 copies (0.3 mol) of dimethylchlorosilanes, and 84.6 copies (0.4 mol) of phenylchlorosilanes. It was dropped under stirring of what was dissolved in the reaction, and the hydrolysis reaction was performed. After stopping stirring 40 minutes after dropping, moving reaction mixture to a separating funnel and settling it. By removing the water and chloride which carry out liquid separation removal of the lower layer hydrochloric acid water divided into the bilayer, next remain in the toluene solution of the upper organopolysiloxane with superfluous toluene by decompression stripping. The toluene 80% solution (B_2-3) (ingredient) of silanol group content organopolysiloxane of the weight average molecular weight 3,000 [about] was obtained. In the above-mentioned preparing method, a molecular weight is GPC (gel permeation chromatography) (measuring apparatus species name: HLC-8020, TOSOH CORPORATION make). It is the weight average molecular weight of the standard polystyrene conversion searched for. Future molecular weights were also measured in the similar way.

(C_2) (ingredient) — a solid formula (III) — a straight-chain-shape polyoxaloxanediol (polydimethyl siloxane diol) which R² is CH₃ inside and has the weight average molecular weight (Mw) shown in Tables 1 and 2.

[0078]

(D_2) (ingredient): N-beta-aminoethyl gamma-aminopropyl methyl dimethoxysilane or N-beta-aminoethyl gamma-aminopropyl triethoxysilane.
(preparing method of top coat) By the combination shown in Tables 1 and 2, top coat was obtained by carrying out mixed stirring of the above (A_0) , (B_2) , (C_2) and (D_2) the ingredient.

(Coating method of top coat) All were painted with the air spray (coating pressure of 2.5 kg / cm²; the latex spray gun W-58 (H) is used).

(Dry curing method of top coat)
[0079] In ordinary temperature dry hardening (for about 20 * and three days).

[0080] Inerters 6–8 Stoving hardening (for 30 * and 20 minutes).

(Validation method of a contamination-resistant coated plate) The method shown below estimated the contamination-resistant coated plate, and the result was shown in Tables 1 and 2.

[0080(1)] The 1 contamination method of contamination-resistant *****: 24-hour neglect after writing a character by the dry magic.

Validation method: Visual observation of the adhesion grade of magic and the state of a character was carried out, and the following three-stage estimation.

O: magic is crawled and it cannot read as a character.

[0081]*: Although magic is crawled, it can read as a character.

* Magic is not crawled but a character can also be deciphered clearly.

(2) Two coated plates of contamination-resistant ***** were installed to the 30-degree inclination exposure test fume, and the direct weathering test was done.

[0082] Validation method: By a color difference meter, it is a colorimetry (XYZ display) about a coated plate. Exposure conditions: For south, a 30-degree inclination (JIS).

[0083] Validation method: [first stage] — Y value after a Y₀ atmospheric exposure test: Y contamination rate: if $D = D_0 - (D_0 - Y_0) \times 100$ — the soiling degree of a coated plate is expressed by this formula, and a soiling degree is so low that a D value is small. The result of the contamination rate six months after exposure was shown in Tables 1 and 2.

[0083(3)] Magic was wiped off with the dry waste cloth after the stain testing by the dry magic tried with the 1 above (1) of decontamination ***** and visual observation of the remaining condition of the magic marker was carried out. A result is based on the following three-stage evaluation.

O: a magic marker can be wiped off thoroughly.

[0084]

*: The magic marker back remains.

x: A magic marker cannot be wiped off.

(4) Dirt was wiped off with the dry waste cloth after the six-month direct weathering test tried with the 2 above (2) of decontamination ***** and visual observation of the remaining condition of dirt was carried out. A result is based on the following three-stage evaluation.

[0085]

*: Dirt can be wiped off thoroughly.

x: Dirt remains a little.

*: Dirt remains a little.

(5) The accelerated weathering test was done with the weathering evaluation sunshine weatherometer for 2000-hours, and visual observation of the state of a coat was carried out. A result is based on the following three-stage evaluation.

[0086]

O: abnormalities are not observed in a coat at all.

*: Gloss retention decreases a little and a crack arises at the end of a base material.

x: A crack and separation arise in the whole base material.

(6) The hardness of the paint film surface was measured by the pencil scratch test of pencil hardness test JIS-K5400 of a paint film surface.

By the combination test was produced by the same method as Embodiment 1 except having produced top coat — the coated plate shown in Table 2, without adding a comparative example 1— (C_2) ingredient. Then, aforesaid embodiment 1—(6) was evaluated.

[0087] — By the same method as Embodiment 1, the coated plate was produced except having used the

http://www4.lipintip.jp/cgi-bin/ren_wsb.cgi?file=nttt035292Fwv44.pdf&ip=20. 2010/10/19

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1.This document has been translated by computer. So the translation may not reflect the original precisely.

2+*** shows the word which can not be translated.

3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing.1]The sectional side elevation showing one embodiment of the contamination-resistant coated plate concerning this invention.

[Explanations of letters or numerals]

1 Base material

2 Primer layer

3 Finishing coat

[Translation done.]